Bayer CropScience

Measuring and Estimating Concentrations of Pesticides in Drinking Water: A Historical Perspective

Presentation to the
Exposure Modeling Public Meeting

March 20, 2012

Outline

- Introduction
- Monitoring versus Standard Risk Assessment
- Most Vulnerable Watersheds
- Historical Approaches to Risk Assessments
- Potential for Refined Risk Assessments

Introduction

- The Food Quality Protection Act (1996) requires risk assessments to include the contribution of pesticide residues in drinking water to dietary assessments.
  - Triggered work by EFED to define both modeling and monitoring assessment procedures
    - By the late 1990's EPA had developed (sometimes informal) guidelines for performing screening assessments and conducting monitoring studies.

Introduction

- While drinking water assessments cover both ground and surface water, this presentation will address only surface water.

- The initial screening assessments were intentionally conservative.
  - Unfavorable screening assessments created the need for refined assessments and monitoring.

Introduction

- Industry initiated drinking water monitoring studies to provide realistic exposure estimates for risk assessment.
  - Initial designs modified as a result of ILSI and WARP projects
- EPA also refined drinking water exposure assessment procedures.
  - Index reservoir and PCA (percent crop area) introduced
  - Probabilistic assessments based on daily values estimated using 30 years of weather data

Introduction

- The drinking water exposure assessment procedures have not changed significantly in the last 10 years.

- The large difference between the predictions from standard assessments and monitoring results demonstrates the overly conservative nature of drinking water assessments.

Monitoring Versus Standard Assessment

- The following slides illustrate the differences between the EPA standard assessment and drinking water monitoring studies (from surface water) conducted by Bayer CropScience.
- Monitoring study designs
  - Highest use watersheds
  - Biweekly or weekly monitoring
  - Three year study (two years for bromoxynil)
  - Finished samples if residues above LOQ in raw water

Monitoring Versus Standard Assessment

- Table definitions
  - Maximum concentration:
    - Monitoring: highest concentration observed in any sample (all sites and all years)
    - Assessment: 1 in 10 year annual maximum value
  - Max TWA (finished)
    - Monitoring: maximum annual time weighted concentration using finished values when available (all sites and all years)
    - Assessment: assuming no losses during treatment

Monitoring Versus Standard Assessment

- Table definitions (continued)
  - Max TWA (raw): maximum time weighted concentration over the three year study period using only concentrations from raw samples (all sites)-iprodione only

Monitoring Versus Standard Assessment

	Concentrations (ppb)		
	Maximum		Max TWA
	Raw	Finished	Finished
Aldicarb (28 sites, 2426 samples)			
Assessment	0.95-17	-	0.17-5.8
Monitoring	0.68	0.24	0.007
Bromoxynil (16 sites, 543 samples)			
Assessment	11	-	0.2
Monitoring	0.38	0.11	0.01

Monitoring Versus Standard Assessment

	Concentrations (ppb)		
	Maximum		Max TWA
	Raw	Finished	Finished
Carbaryl (20 sites, 2369 samples)			
Assessment	47-745	-	1.9-31
Monitoring	0.040	0.16	0.005
Ethoprophos (5 sites, 448 samples)			
Assessment	15-127	-	2.6-13
Monitoring	0.012	ND(<0.003)	(<0.003)

Monitoring Versus Standard Assessment

	Concentrations (ppb)		
	Maximum		Max TWA
	Raw	Finished	Finished
Oxadiazon turf (3 sites, 693 samples)			
Assessment	52	-	19
Monitoring	0.17	0.13	0.025

Monitoring Versus Standard Assessment

	Concentrations (ppb)		
	Maximum		Max TWA
	Raw	Finished	Raw
Iprodione turf (3 sites, 587 samples)			
Assessment	361	-	1.6
Monitoring	0.60	0.16	0.037
3,5-DCA (iprodione metabolite)			
Assessment	153	-	36
Monitoring	<0.032	<0.035	(<0.025)

Missed the Peak

- A common response to the difference between standard assessment results and monitoring results is that the sampling was not frequent enough to observe the peak concentrations.
  - Potentially true in some cases
  - In most cases, the concentrations do not match over a significant portion of the concentration distributions.
    - This is shown with the distribution of the results from each sampling interval from the carbaryl study and the distribution of daily modeling values.

Comparison of Distributions

	Carbaryl Concentration (ppb) at Specified Percentile					
Percentile	**50**	**70**	**90**	**95**	**99**	**Max**
Assessment						
oranges	<0.001	0.018	20.4	44.6	140	745
apples	0.002	0.040	3.2	7.7	15	66
Monitoring Study						
raw	ND	ND	ND	0.003	0.017	0.04
raw and finished	ND	ND	ND	ND	0.005	0.16

Special Cases

- Assessments for rice and cranberries result in especially conservative assessments.
  - Assume direct spray to paddy or bog water
  - Water in the rice paddy or cranberry bog is essentially considered as drinking water.

Most Vulnerable Watersheds

- The WARP research (discussed later) identified use intensity (mass of active ingredient/area of watershed) as the most important factor in its regression equations.
  - High use intensity occurs in watersheds where the product is applied to most of the watershed area.
    - Highest use intensity often occurs in small watersheds composed mainly of agricultural fields.
  - Other factors may be important in determining vulnerability between watersheds of similar use intensity

Most Vulnerable Watersheds

- Variability of concentrations
  - Concentrations in flowing water are more variable than in lakes and reservoirs.
    - As a result of the decreased variability, sampling can be less frequent for lakes and reservoirs.
  - Smaller streams tend to be more variable than larger rivers.

Most Vulnerable Watersheds

- Small streams are not a source of drinking water because of low flow during dry periods.
  - Damming a small stream may provide enough storage to provide continuous drinking water

- Small reservoirs in watersheds composed largely of agricultural fields tend to be the most vulnerable watersheds.
  - EPA's Index Reservoir is an example of a vulnerable watershed.

Historical Approaches-Assessment

- Farm Ponds
- Index Reservoir
- SWMI (Surface Water Mobility Index)
- WARP (WAtershed Regressions for Pesticides)

Farm Ponds and Index Reservoir

- At first EPA used the farm pond ecological scenario to estimate concentrations in drinking water.
- EPA changed the farm pond into a reservoir and incorporated a PCA (percent crop area) factor for crops.
  - Not applied for rice and cranberries
- The meta-model FIRST was developed to provide an upper bound screening value.

Farm Ponds and Index Reservoir

- EPA worked with USGS to conduct monitoring at a number of Index Reservoirs around the country.
  - Resulting concentrations were much lower than predictions (probably because of use intensity).

SWMI-Surface Water Mobility Index

- Wenlin Chen developed a regression procedure to predict concentrations in surface water.
- Concentration distributions were developed for a reference compound (atrazine) in reference watersheds as a function of use intensity.
- Concentrations of other compounds are estimated by multiplying by a surface water mobility index SWMI (function of half life and k_{oc})

$$\boldsymbol{SWMI} = \frac{\boldsymbol{e}^{-3.466\,/\,T_{1/2}}}{\left(1 + 0.00348\,\boldsymbol{K_{oc}}\right)}\left(1 + 0.00026\boldsymbol{K_{oc}}\right)$$

WARP-Watershed Regressions for Pesticides

- USGS regression model for estimating concentration statistics in surface water
  - Provides estimated concentrations for nine percentiles for a single compound
    - 95th, 90th, 80th, 75th, 50th, 25th, 15th, 10th and 5th
- A number of regression models have been developed
  - Single compounds
  - Multi-compound (based on SWMI)

WARP

- Variables for multi-compound WARP
  - Use intensity
  - SWMI
  - Vapor pressure factor
  - Percent C and D soils in watershed
  - Dunne overland flow
  - May and June rainfall

WARP

- A key finding is use intensity explained 50-70 percent of the variability in the measured data.
    - USGS developed a procedure for estimating use intensity in watersheds used to supply drinking water

Implementation of WARP

- Scientists from four organizations (EPA, USGS, USDA, and CropLife America) worked on a project to develop procedures for implementing WARP in estimating drinking water residues for dietary risk assessments.
  - Started in 2000 and continued through about 2006
- Accomplishments - Monitoring
  - Conducted a monitoring program which helped assess sampling frequencies needed for flowing water streams

Implementation of WARP

- Accomplishments - Assessment
  - Developed two procedures for estimating watershed-specific daily concentrations with appropriate temporal associations suitable for use in dietary risk assessments
  - Developed a procedure for conducting regional cumulative assessments involving multiple community water systems
- EPA was unable to continue development of WARP for drinking water assessments due to non-technical reasons.

Potential for Refined Assessments

- Because standard assessments appear to be overly conservative when compared to monitoring data, refined approaches are necessary.

- Two approaches
  - Methodology for acceptance of monitoring studies
  - Refined assessment procedures

Acceptance of Monitoring Studies

- Differences between standard assessments and targeted monitoring data can be greater than two orders of magnitude
  - Monitoring now often rejected due to “missed the peak” argument
  - Potential solution is the application of bias factors
    - This has been a subject of discussion in the atrazine SAP meetings

Refined Assessments

- Potential approaches
  - Use of refined use information
  - Option to evaluate all relevant community water systems rather than a hypothetical index reservoir
    - This can be helpful for crops with limited geographical extent (for example, products used on rice and cranberries or on geographically limited pests).
  - Flexibility to consider other factors when relevant
    - Other kinetics than single first order
    - Vegetative buffer strips when required by the label
    - Other case-specific factors

Refined Use Data

- As mentioned for WARP, use intensity is an important variable so a realistic assessment depends on having an accurate estimate of use.
- Use intensity is composed of three factors:
  - PCA (percent cropped area)
  - PCT (percent crop treated)
  - Typical annual application rate
  - All three factors have been used in cumulative assessments.
    - The use factors used in cumulative assessments have varied.

Refined Use Data

- Sales data is another potential source of information on use intensity
- The difference between standard assessments and monitoring data narrows considerably when accurate use intensities are used.
  - For example, in the iprodione turf example (sales data available for individual watersheds) the use intensity assumed in the standard assessment was a factor of 58 higher than in the U.S. watershed with the highest use intensity

Conclusions

- Standard assessments of residues in drinking water are overly conservative as shown by comparisons with targeted monitoring data.
- Use of more realistic use intensities will provide more realistic, yet conservative exposure estimates.
- Use of bias factors and similar approaches can be used to quantify potential uncertainty in monitoring data to allow their use in higher tier assessments.